

California Regional PM₁₀ and PM_{2.5} Air Quality Study (CRPAQS)

Statement of Work – CRPAQS Data Analysis Task 6.1 ANALYSIS OF THE PHASE DISTRIBUTION OF PM AND PM PRECURSORS

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Sonoma Technology, Inc.**

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Introduction

Ambient concentrations of particulate matter (PM) exceed health-based air quality standards in central and southern California. The development of effective emissions control strategies to mitigate this problem requires an understanding of the chemical and physical phenomena that cause high air pollution concentrations. One factor associated with high PM levels is a shift of the gas-aerosol partitioning toward the aerosol species during winter air pollution episodes. Improved characterization of the phase distributions of PM and PM precursors is likely to advance the understanding of the phenomena that cause unhealthy air quality.

The phase partitioning of atmospheric PM and gaseous co-pollutants is complex and believed to be dependent on many factors, including meteorological conditions, atmospheric chemical composition and chemistry, and air mass history. Gas-aerosol partitioning often shifts more toward the aerosol species, which elevates PM concentrations, during winter air pollution episodes in California than at other times of the year. This is especially true in California's San Joaquin Valley (SJV) where multi-day periods with stagnant cool moist atmospheric conditions often occur in winter. The detailed aerometric data collected during the measurement phase of CRPAQS provide an opportunity to advance the scientific understanding of pollutant phase partitioning in general and, specifically, winter air pollution episodes in the SJV. A descriptive and interpretive data analysis study has been designed to address the following phase-partitioning-related questions:

1. What is the distribution of PM (including chemical composition) and precursor species among phases (gas, liquid, and aerosol)?
2. What chemical and physical mechanisms contribute to the observed phase distributions?
3. How do the phase distributions and chemical and physical mechanisms vary in space and time?
4. How do the phase distributions and chemical composition vary before, during, and after fog events?

The answers to these questions are important for understanding secondary aerosol problems and for selecting effective control strategies to reduce wintertime episodic PM levels in the region. The results of the analyses are likely to be important for refining the conceptual model and for specifying the chemical and physical processes that need to be included in the atmospheric models that are used to model these data and candidate emission control strategies.

Scope of Work

The extensive spatial and temporal coverage for PM and PM precursors in the CRPAQS aerometric database offers a unique opportunity to better characterize the phase partitioning of key species in the SJV. IMS-95 data (Kumar et al., 1998) provided a snapshot of both summertime and wintertime phase partitioning of inorganic species in the SJV/AUSPEX data (Chow et al., 1998). Strader et al. (1999) and Schauer and Cass (2000) also provided a snapshot of the organic phase partitioning in urban areas. The scope of work for Task 6.1 will include a comprehensive description of phase partitioning across space and time and address the obvious spatial/temporal limitations of the earlier work. The phase partitioning results will afford interpretations of the relevant physical and chemical processes governing the formation and, to a lesser extent, the removal of PM.

For this task, STI will acquire all the relevant gaseous and aerosol concentration data for the CRPAQS anchor and satellite sites, the fogwater chemistry data where available, and the relevant surface meteorological data from the CRPAQS master database. We will primarily use the 1-hr and 24-hr average data. These data will be incorporated into a database suitable for the partitioning analyses. The database will include NO_x -, NH_3 -, SO_2 -, and organic-emissions-related components and the oxidant components. The measured components associated with each type of precursor emissions are defined as follows.

- NO_x -related: NO , NO_2 , HNO_3 , PAN, $\text{PM}_{2.5}\text{-NO}_3$, $\text{PM}_{2.5-10}\text{-NO}_3$, and NO_3 fog
- NH_3 -related: NH_3 , $\text{PM}_{2.5}\text{-NH}_4$, $\text{PM}_{2.5-10}\text{-NH}_4$, and NH_4 fog
- SO_2 -related: SO_2 , $\text{PM}_{2.5}\text{-SO}_4$, $\text{PM}_{2.5-10}\text{-SO}_4$, and SO_4 fog
- Organics: light hydrocarbons, aldehydes, heavy hydrocarbons, $\text{PM}_{2.5}\text{-OC}$, $\text{PM}_{2.5-10}\text{-OC}$
- Oxidants: ozone and H_2O_2

The component concentrations will be converted to common units (e.g., $\mu\text{g}/\text{m}^3$ of nitrogen, sulfur, or carbon) to facilitate comparisons. It is recognized that the components are not available from all sites and time periods, but many are available for the winter intensive from the anchor sites at Bakersfield, Angiola, Fresno, Sierra Nevada Foothills, Modesto, San Jose, and Bethel Island; some are available for the annual program. Generally, the gaseous data are more limited than the particle data, since very few sites have SO_2 analyzers or hydrocarbon/aldehyde sampling. Most of the satellite sites lack NO_x , SO_2 , or VOC gaseous concentration data. Yet, many satellite sites have HNO_3 , $\text{PM}_{2.5}$ NO_3 , NH_3 , and $\text{PM}_{2.5}$ NH_4 . The most spatially, temporally, and chemically complete data are likely to be available from the winter and summer intensive data collection periods, so our analyses will focus on these periods.

Our planned approach involves using as much data as possible to address phase-partitioning issues, recognizing that data are not uniformly available.

1. The full phase distribution of nitrogen species (NO_x and NH_3 -related) at those anchor sites and time periods with sufficient data will be examined. These will, for the most part, be limited to the winter intensive time periods. Since NO_y data are available for more sites and times of year than NO_y and nitric acid data, we will also examine distribution of NO , particulate NO_3 , and the remaining oxidized nitrogen species (NO_y - NO - particulate NO_3) to assess the seasonality of the NO_x -related nitrogen species distributions. The sulfur- and organic-species distributions will be examined for a more limited set of locations. In fact, there is only one SO_2 analyzer in the SJV, and both the SO_2 and SO_4 levels are quite low compared to NO and particulate NO_3 . The nitrogen-, ammonia-, and organic-species phase distributions will provide the informative comparisons of precursor species versus product species, and gaseous products versus aerosol products by site and time period.
2. With the extensive network of MiniVol samplers, there are many more locations for which phase partitioning of the HNO_3 , NH_3 , and $\text{PM}_{2.5}\text{-NH}_4\text{NO}_3$ components can be evaluated. We will examine the ratio of aerosol nitrate to total nitrate and the ratio aerosol ammonium to total ammonia by season and location. We think this is one of the most important elements of this task because the results may have implications for the extent of conversion of NO_x emissions to particulate NO_3 . This is important scientifically because the relative abundance of nitric acid and ammonia indicates which types of emissions are likely to control the ambient levels of NH_4NO_3 aerosol. These results may contribute to the conceptual model for nitrate in the SJV.
3. There is an opportunity to examine the highly time-resolved continuous nitric acid and aerosol nitrate data from the continuous analyzers at the Angiola, Sierra Nevada Foothills, and Fresno First Street sites. We are aware of the data quality concerns for the continuous nitric acid data for all periods and for the aerosol nitrate data during periods with abnormally high shelter temperatures. Our use of the highly time-resolved continuous nitric acid and aerosol nitrate data will be restricted to the periods and locations that we believe provide valid data. These data offer an opportunity to probe for periods with chemical formation of oxidized NO_x and for periods of changing gas-aerosol partitioning. Our approach will be to focus on periods with lighter winds where transport may be a less important factor than local chemical formation and phase-shifting. The data will be stratified in a number of ways, including day versus night, warm versus cool, moist versus dry, and low NO_y versus high NO_y , to assess which parameters may influence nitric acid production and partitioning.
4. All these data will be interpreted in light of known chemical mechanisms. We will look for evidence of the importance of the daytime photochemical mechanism, the nighttime HNO_3 mechanism, and the aqueous sulfate production mechanism. Spatial and temporal differences in the relative importance of various mechanisms will be assessed. The extent to which the data support or refute the mechanisms will be evaluated. For example, Watson and Chow (2002) postulated that the nighttime nitric acid formation mechanism was active aloft in the SJV and responsible for the spatial uniformity of secondary nitrate in winter. Nighttime NO , NO_2 , ozone, nitric acid, and nitrate concentration data from elevated sites, like the Sierra Nevada Foothills station, will be

examined for evidence of conversion of NO_x to nitric acid and nitrate at night. In addition, we will investigate the gas-aerosol partitioning of nitric acid and nitrate because the existing inorganic thermodynamic models do not explain why nitric acid co-exists with high ammonia levels during cool, moist conditions in the SJV. We will apply the SCAPE2 model, as was done with the IMS-95 data, to assess the consistency of the data. We will explore the data to assess what factors might explain discrepancies and deserve further study in the laboratory or the field.

5. We will prepare a manuscript describing the methods and results of analyses carried out under this task. This manuscript may cover more than one task. Presentation material will be prepared that incorporate the manuscript and additional tables, figures, and discussion items. The results will be presented at a west coast conference, such as the American Aerosol Association Research Conference scheduled for fall 2003.

Time Line

The schedule for this work depends on the availability of the overall CRPAQS data set which we assume will be available in early 2003. After we are notified that the database and documentation are available, there will be a two-month period during which the phase distribution database will be assembled and reviewed. Analysis of these data will occur during the following two months. Preparation of the manuscript and presentation material will occur during the final two-month period. We anticipate that this six-month effort will occur in February–July of 2003.

Schedule of Deliverables

Table 1 lists the deliverables to be prepared under Task 6.1 and their planned due dates.

Table 1. Schedule of deliverables.

Deliverable	Deliverable Due Date
Final work plan	January 2003
Progress reports	Monthly
Draft manuscript	July 31, 2003
Final manuscript	August 31, 2003

Description of Deliverable(s)

The deliverables for this task consist of a final work plan; monthly progress reports that describe the technical progress, how unexpected problems are being handled, and budget expenditures; and a manuscript that describes the methods and results of analyses carried out under this task.

ARB Staff Assigned to This Task

The ARB Project Manager assigned to this Task is:

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STI Staff Assigned to this Task

The STI Project Manager is Lyle R. Chinkin. The STI Task Manager assigned to Task 6.1 is Frederick W. Lurmann.

Percentage of Work, Data Products To Be Performed/Delivered by ARB

None required.

Software and Models to Be Used by STI

Inorganic thermodynamic models such as SCAPE2 and AIM.

Models, Reports, or Other Data to Be Supplied to STI by ARB

None required.

References

- Chow J.C., Watson J.G., Lowenthal D.H., Egami R.T., Solomon P.A., Thuillier R.H., Magliano K.L., and Ranzieri A. (1998) Spatial and temporal variations of particulate precursor gases and photochemical reaction products during SJVAQS/AUSPEX ozone episodes. *Atmos. Environ.* **32(16)**, 2835-2844.
- Kumar N., Lurmann F.W., Pandis S., and Ansari A. (1998) Analysis of atmospheric chemistry during 1995 integrated monitoring study. Report prepared for the San Joaquin Valleywide Air Pollution Study Agency, c/o the California Air Resources Board, Sacramento, CA by Sonoma Technology, Inc., Petaluma, CA, STI-997214-1791-FR, July.

- Schauer J.J. and Cass G.R. (2000) Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environ. Sci. Technol.* **34**, 1821-1832.
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- Watson J.G. and Chow J.C. (2002) A wintertime PM_{2.5} episode at the Fresno, CA, Supersite. *Atmos. Environ.* **36**, 465-475.